

**357.** *The Atom Polarisation of Some Co-ordination Compounds of Metals.*

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The dielectric constants, specific volumes, and refractive indices of benzene or dioxan solutions of the aluminium and the ferric complex of acetylacetone, the beryllium and the ferric derivative of dibenzoylmethane, and of a number of *trans*-planar complexes of copper and nickel have been measured at 25°. The differences between  $P_2$  and  $[R_D]$  derived from these results are interpreted as atom polarisations arising principally from bending vibrations in which the chelate rings act as units. By making certain assumptions regarding the effective electric moments of the vibrating units, the apparent force constants of these vibrations have been calculated. The results are discussed in relation to the flexibility of the molecule, and arguments are given in favour of their interpretation as atom polarisation rather than as arising from the presence of permanent dipole moments in the molecules as a whole.

IN 1932 it was observed<sup>1</sup> that the molecular polarisations ( $P$ ) of basic beryllium acetate and the acetylacetone complex of beryllium in benzene or carbon tetrachloride solution exceed their molecular refractions ( $[R]$ ) by about 30 c.c. As evidence had been obtained that some other compounds with highly dipolar bonds, such as co-ordinate linkages, had rather large atom polarisations ( ${}_A P$ ), and since crystal-structure measurements indicated that the basic beryllium acetate molecule is symmetrical, it was suggested that the  $P - [R]$  differences were due to high  ${}_A P$  values, and not to the presence of permanent dipole moments in the molecules.

Although initially this interpretation was not generally accepted, confirmation of the

<sup>1</sup> Smith and Angus, *Proc. Roy. Soc., A*, **137**, 372.

results was obtained when Finn, Hampson, and Sutton<sup>2</sup> obtained similar  $P - [R]$  differences for acetylaceton complexes of beryllium and other metals in various solvents. Coop and Sutton<sup>3</sup> showed that these differences also exist in the vapour state, and, from exhaustive consideration of factors which might give rise to them, it was inferred that the original explanation was correct.

The Sellmeier dispersion equation, statistical arguments,<sup>4</sup> and simple geometrical treatment of the mechanics of the molecules<sup>5</sup> all indicate that  ${}_A P$  can be expressed in terms of the force constants ( $k$ ) associated with the various modes of vibration of the molecules and the effective charges ( $e_e$ ) displaced during these vibrations by the relation :

$${}_A P = \sum_i (4\pi N e_{ei}^2 / 9k_i)$$

Hence the largest contributions to  ${}_A P$  come from the vibrations of low force constant, and, in the absence of low-frequency torsional vibrations, these will be bending vibrations. For a single such bending vibration the contribution to  ${}_A P$  is  $4\pi N e_{ei}^2 / 9k_i = 4\pi N e_{ei}^2 R_i^2 / 9R_i^2 k_i = 4\pi N \mu_i^2 / 9k_{bi}$ , where  $R_i$  is the effective length of the vibrating system,  $k_{bi}$  is the force constant of the bending vibration in erg/radian<sup>2</sup>, and  $\mu_i$  is the electric moment of the vibrating unit. Hence, if the molecule has one type of bending vibration with a particularly low force constant,  ${}_A P$  is given very closely by  ${}_A P = 4\pi z N \mu_1^2 / 9k_b$  where  $z$  is the number of degenerate one-dimensional vibrational modes of this type associated with the molecule.

Coop and Sutton<sup>3</sup> pointed out that for the metal-acetylaceton complexes the vibrations likely to determine the value of  ${}_A P$  are those associated with the vibration of the rings, as units, relative to the remainder of the molecule. In tetrahedral, octahedral, and cubic complexes, therefore, the chelate groups can be regarded as acting as 2, 3, and 4 one-dimensional vibrators, respectively. Hence, if the force constants  $k_b$  and electric moments  $\mu_1$  associated with the ring systems are of the same order of magnitude in each case, the  ${}_A P$  values for these three groups of compounds would be expected to be approximately in the ratio 2 : 3 : 4. The experimental results show this to be the case.

Since systematic studies of compounds of this type have been largely confined to the metal-acetylaceton complexes, polarisation measurements have now been made on solutions of other co-ordination compounds in which similar behaviour is to be expected. In the absence of the possibility of studying them in the vapour state, it would have been preferable to use only carbon tetrachloride or benzene as solvent for these compounds. Only a few of them, however, are sufficiently soluble in these solvents to permit their study with any reasonable degree of accuracy; but it has been found that for co-ordination compounds studied both in benzene and in dioxan only slightly higher  $P_2$  and  $P_2 - [R_D]$  values are obtained when the latter solvent is used. The range of compounds investigated has therefore been extended by using dioxan as solvent when the solubility in benzene was found to be too low for useful measurements to be made. The compounds now studied include the aluminium and the ferric complex with acetylaceton, the beryllium and the ferric derivative of dibenzoylmethane, and a number of planar complexes of copper and nickel.

The direct determination of the molecular refractions of some of these compounds proved difficult. In many cases the solutions were highly coloured, a factor which not only rendered the refractive index measurements difficult, but also threw doubt upon the value of the results owing to the incidence of anomalous dispersion. In such cases, therefore, the  $[R_D]$  values have been calculated from the molecular refractions of the parent organic compounds, the contributions from the metal atoms and the bonds associated with them being taken as the mean values found for these contributions in compounds for which the measurements did not seem to be vitiated by anomalous dispersion: the allowance made was 12 c.c. for both copper and nickel.

The results are summarised in Table 1, where  $\alpha$ ,  $\beta$ , and  $\gamma$  are the limiting values of

<sup>2</sup> Finn, Hampson, and Sutton, *J.*, 1938, 1254.

<sup>3</sup> Coop and Sutton, *J.* 1938, 1269.

<sup>4</sup> Davidson and Sutton, *J.*, 1939, 347.

<sup>5</sup> Barriol and Regnier, *J. Chim. phys.*, 1952, 49, 213.

$d\epsilon/dw$ ,  $dv/dw$ , and  $dn^2/dw$ , respectively, at zero concentrations.  $[R_D]$  values calculated as described above are shown in square brackets.

The measurements on aluminium and ferric complexes with acetylacetone confirm those of Finn, Hampson, and Sutton,<sup>2</sup> especially in showing that for the latter compound  ${}_A P$  is rather greater than would be expected from the values for other compounds of the type

TABLE I. Summary of polarisation data.

Compound	Solvent	$10^3\alpha$	$-10^3\beta$	$10^3\gamma$	$P_{2\infty}$ (c.c.)	$R_D$ (c.c.)	$P_{2\infty} - R_D$ (c.c.)
Aluminium-acetylacetone	Benzene	861	310	140	133	88	45
	Dioxan	1121	121	317	139	88	51
Ferric-acetylacetone	Benzene	1056	373	281	151	99	52
	Dioxan	1337	190	448	158	99	59
Beryllium-dibenzoylmethane	Benzene	910	343	564	187	156	31
	Dioxan	1130	159	795	192	159	33
Ferric-dibenzoylmethane	Benzene	1130	386	525	318	238	80
	Dioxan	1440	187	745	336	242	94
Aluminium-diethyl malonate	Benzene	754	288	-50	200	120	80
<i>trans</i> -Copper-salicylaldehyde	Dioxan	2000	356	625	154	82 [86]	68
<i>trans</i> -Copper-salicylidene-methylamine...	Dioxan	1562	273	534	153	91	62
<i>trans</i> -Copper-salicylidene- <i>p</i> -chloroaniline	Dioxan	1180	297	630	204	147 [151]	53
<i>trans</i> -Copper-salicylidene- <i>p</i> -bromoaniline	Dioxan	994	390	570	203	154 [157]	46
<i>trans</i> -Copper-salicylidene- <i>p</i> -iodoaniline	Dioxan	965	429	559	224	169 [169]	55
<i>trans</i> -Copper-3-hydroxy-1 : 3-diphenyl-triazene	Dioxan	860	267	770	168	155 [155]	13
<i>trans</i> -Copper-salicylaldoxime	Dioxan	858	350	470	108	81 [86]	22
<i>trans</i> -Nickel-salicylaldoxime	Dioxan	1127	373	440	117	76 [86]	31
<i>trans</i> -Nickel-phenylazo- <i>p</i> -cresol	Benzene	879	418	—	175	[149]	26
<i>trans</i> -Nickel-2-phenylazopyrrole	Benzene	791	491	—	137	[116]	21

$M(\text{acac})_3$ . Coop and Sutton<sup>3</sup> attributed this to either a large effective moment of the vibrating unit or a small force constant, both of which effects would follow if the bonds to the central atom were unusually polar in character. It is of interest, therefore, that the  $P_2 - [R_D]$  value for ferric complex of dibenzoylmethane is much greater even than that for the acetylacetone complex. That this is not due to a large additional moment within the ligand is shown by the fact that the  ${}_A P$  value for the beryllium complex of dibenzoylmethane is almost the same as for that with acetylacetone. This result, therefore, seems to support Coop and Sutton's explanation, since the more highly polarisable dibenzoylmethane structure would tend to favour an increased polarity in the bonds to the central atom. It was impossible to follow this matter further, as the other metallic derivatives of dibenzoylmethane which were prepared were too sparingly soluble to permit their study.

For aluminium-diethyl malonate the difference between  $P_2$  and  $[R_D]$  is appreciably greater than for other complexes of aluminium, and hence it probably includes a contribution from orientation polarisation arising from rotation of the ethoxy-groups. The  $P_2 - [R_D]$  differences for the planar complexes of copper and nickel are much smaller than would correspond with the orientation polarisation of the *cis*-compounds, and can therefore be interpreted as being the  ${}_A P$  values for the *trans*-modifications, confirming the general conclusion that when only one form of a complex can be isolated this is usually the *trans*-modification.

In order to calculate the force constants for the vibration of the rings as units it is necessary to make some assumptions regarding the effective dipole moments of the vibrating groups. For this purpose the value (7.5 D) assumed by Coop and Sutton<sup>3</sup> in calculating the force constants for the acetylacetone complexes has been taken as a basis. By assuming the bonds to the central atom to be similar in each case, the modifications to this value introduced through the replacement of oxygen by nitrogen, and by the addition of polar substituents, have been assessed from the appropriate bond and group moments.

As was done by Coop and Sutton, the chelate groups in the tetrahedral and octahedral complexes have been regarded as acting as two and three one-dimensional vibrators, respectively. In the planar complexes, however, the vibrations of the two rings involve a

folding or twisting of the molecule as a whole, so they have been treated as single one-dimensional vibrators. As  $k_b = 4\pi z N \mu_1^2 / 9 \Delta P$ , it follows, by insertion of the values of the universal constants, that  $k_b = 0.841 \times 10^{-12} \times z \mu_1^2 / \Delta P$  erg/radian<sup>2</sup>, where  $\mu_1$  is expressed in D and  $\Delta P$  in c.c.

The values of  $\mu_1$  assumed for the various compounds and the apparent values of the vibrational force constants derived from them are shown in Table 2, which also includes a similar interpretation of previous measurements on analogous compounds. In computing the values of  $\Delta P$  for the *trans*-forms of the nickel-glyoxime complexes, allowance has been made for the contributions to the molecular refraction of the nickel atom and of the bonds

TABLE 2. *Atom polarisations and bending force constants for co-ordination compounds.*

Compound	$\Delta P$ (c.c.)	Ref.	$\mu_1$ (D)	$10^{12} k_b$ (erg/radian <sup>2</sup> )
Beryllium-acetylacetonone .....	24	1	7.5	3.9
	27	2	7.5	3.5
Beryllium-dibenzoylmethane .....	31	*	7.5	3.1
Aluminium-acetylacetonone .....	40	2	7.5	3.6
	45	*	7.5	3.2
Ferric-acetylacetonone .....	57	2	7.5	2.5
	52	*	7.5	2.8
Ferric-dibenzoylmethane .....	80	*	7.5	1.8
Chromium-acetylacetonone .....	40	2	7.5	3.6
Cobaltic-acetylacetonone .....	30	2	7.5	4.5
<i>trans</i> -Copper-salicylaldehyde .....	68	*	7.5	0.7
<i>trans</i> -Copper-salicylidene-methylamine .....	54	7	7.2	0.8
	62	*	7.2	0.7
<i>trans</i> -Copper-salicylidene- <i>p</i> -chloroaniline .....	53	*	6.7	0.7
<i>trans</i> -Copper-salicylidene- <i>p</i> -bromoaniline .....	46	*	6.7	0.8
<i>trans</i> -Copper-salicylidene- <i>p</i> -iodoaniline .....	55	*	6.8	0.7
<i>trans</i> -Copper-3-hydroxy-1:3-diphenyltriazene .....	13	*	5.0	1.5
<i>trans</i> -Copper-salicylaldoxime .....	22	*	7.2	2.0
<i>trans</i> -Nickel-salicylaldoxime .....	31	*	7.2	1.4
<i>trans</i> -Nickel-phenylazo- <i>p</i> -cresol .....	26	*	5.3	0.9
<i>trans</i> -Nickel-2-phenylazopyrrole .....	21	*	6.6	1.8
<i>trans</i> -Nickel-methyl- <i>n</i> -propylglyoxime .....	28	6	7.8	1.7
<i>trans</i> -Nickel-methyl- <i>n</i> -butylglyoxime .....	24	6	7.8	2.0
<i>trans</i> -Nickel-benzylmethylglyoxime .....	23	6	7.8	2.1

\* Present work.

associated with it. The figures used, therefore, are 12 c.c. less than the  $P_{2\infty} - [R_D]$  values recorded by Cavell and Sugden.<sup>6</sup>

The results for the aluminium- and the ferric-acetylacetonone compound are in fair agreement with previous data, whilst, in spite of the greater molecular weight of beryllium-dibenzoylmethane, its force constant falls in line with the values found for various acetylacetonone complexes. This observation seems to confirm the essential validity of Coop and Sutton's suggestion that the major contributor to the atom polarisation is the vibration of the rings as relatively rigid units.

The planar compounds so far studied fall into two distinct classes, with force constants lying within the ranges 0.7–0.9 and 1.4–2.1 erg/radian<sup>2</sup>, respectively. The latter group includes all the five-membered ring complexes studied, together with the salicylaldoxime derivatives of copper and nickel. Their  $\Delta P$  values are commensurate with those of tetrahedral complexes. This circumstance, and the fact that although the rings are of very different types the force constants derived are all of the same order, appear to justify the assumption that the rings are essentially coplanar, the main contributions to  $\Delta P$  arising from the vibrations of the rings as units. Unlike the acetylacetonone and dibenzoylmethane derivatives, the rings in some of these compounds are not symmetrical, and so their moments will not act exactly along the bisector of the angle made by their bonds to the central atom. The method of treatment holds good, however, if  $k_b$  is interpreted as the force constant with respect to the distortion of the angle between the ring dipoles.

<sup>6</sup> Cavell and Sugden, *J.*, 1935, 621.

<sup>7</sup> Charles and Freiser, *J. Amer. Chem. Soc.*, 1951, **73**, 5223.

The six-membered ring systems, on the other hand, may not be strictly planar and hence vibrational modes other than the symmetrical vibrations of the two rings may be involved. Such increased flexibility of the system may account for the fact that the  $\Delta P$  values for these compounds are generally much greater than for those containing five-membered rings. The salicylaldoxime complexes seem to be exceptional, but it is possible

TABLE 3. *Polarisation data.*

$10^6 w$	$10^4 \Delta \epsilon$	$-10^6 \Delta v$	$10^4 \Delta n$	$10^6 w$	$10^4 \Delta \epsilon$	$-10^6 \Delta v$	$10^4 \Delta n$	$10^6 w$	$10^4 \Delta \epsilon$	$-10^6 \Delta v$	$10^4 \Delta n$
<i>Aluminium-acetylacetonone in benzene</i>				<i>Ferric-acetylacetonone in dioxan</i>				<i>Beryllium-dibenzoylmethane in benzene</i>			
6028	52	188	3	11,608	155	215	18	4663	40	160	9
13,448	115	423	6	22,020	295	420	35	10,531	93	360	20
19,036	165	584	9	29,560	391	556	46	16,171	148	554	30
27,889	237	861	13	41,337	533	797	65	23,078	203	789	42
34,396	293	1067	16	48,929	655	929	77	27,216	243	925	49
49,313	432	1522	23	60,658	819	1152	96	44,103	303	1520	89
<i>Aluminium-acetylacetonone in dioxan</i>				<i>Ferric-acetylacetonone in benzene</i>				<i>Beryllium-dibenzoylmethane in dioxan</i>			
7470	80	97	8	7485	80	266	7	3748	41	58	10
15,269	158	180	17	16,940	177	636	16	7977	92	127	22
21,998	242	278	24	32,196	339	1216	30	9941	107	153	28
28,771	313	350	32	36,454	387	1369	34	15,394	175	237	42
34,787	392	425	39	42,257	447	1555	—	20,366	234	332	58
56,832	631	698	64	49,819	523	1860	—	30,400	347	485	85
<i>Ferric-dibenzoylmethane in benzene</i>				<i>Ferric-dibenzoylmethane in dioxan</i>				<i>Ferric-dibenzoylmethane in dioxan</i>			
5235	60	71	5	2230	27	88	3	1602	21	30	4
11,188	123	—	11	3750	39	144	5	2680	40	50	7
14,906	172	180	16	5158	56	197	8	4586	68	85	12
25,070	281	302	28	7420	85	295	13	6242	87	118	16
34,811	393	427	40	8507	94	330	14	7695	123	141	20
36,839	418	444	41	11,339	132	429	20	8731	226	165	23
<i>Aluminium-diethyl malonate in benzene</i>				<i>Copper-salicylidene-p-bromoaniline in dioxan</i>				<i>Copper-salicylidene-p-chloroaniline in dioxan</i>			
8741	69	294	— 2	2583	27	102	5	3603	42	101	7
15,905	116	468	— 4	7334	75	288	14	7397	95	209	15
19,940	153	571	— 5	9616	93	372	20	10,256	123	305	21
25,179	183	727	— 5	11,346	105	—	23	14,306	169	440	31
30,793	237	878	— 5	14,042	132	474	48	15,434	182	478	—
				19,740	194	764	—	26,154	308	778	58
<i>Copper-salicylaldehyde in dioxan</i>				<i>Copper-salicylidene-p-iodoaniline in dioxan</i>				<i>Copper-salicylidene-methylamine in dioxan</i>			
1407	24	53	3	2139	18	86	4	3761	59	109	7
2027	40	76	5	4966	39	204	10	6601	—	177	12
3662	69	128	8	6636	68	288	12	9913	153	275	19
4559	93	164	10	11,842	117	499	22	14,145	218	390	27
5847	119	209	12	11,890	117	501	23	19,027	300	516	37
6643	132	236	15	14,630	141	526	30	22,312	350	603	43
<i>Copper-3-hydroxy-1 : 3-diphenyltriazen in dioxan</i>				<i>Copper-salicylaldoxime in dioxan</i>				<i>Nickel-phenylazo-p-cresol in benzene</i>			
4551	39	101	13	3091	27	104	4	5086	46	221	—
9841	85	259	25	4879	44	176	6	10,128	85	423	—
13,678	119	370	38	7585	62	260	12	14,821	128	619	—
18,406	152	492	48	10,394	85	378	18	20,250	178	859	—
21,956	188	—	59	12,677	112	433	20	22,213	198	909	—
26,621	234	697	—								
<i>Nickel-salicylaldoxime in dioxan</i>				<i>Nickel-2-phenylazopyrrole in benzene</i>							
1866	21	—	3	5914	47	285	—				
3459	39	—	6	9517	79	484	—				
5057	58	187	8	12,320	95	579	—				
6561	73	245	10	16,891	132	849	—				

that there may be hydrogen bonds bridging the oxygen atoms in the two rings, somewhat similar to those which occur in glyoxime complexes, which may "stiffen" the vibrating system by imposing a restriction upon the mode of vibration.

That the  $\bar{P}_2 - [R_D]$  differences for the other compounds containing six-membered rings may be due in part to a permanent dipole moment arising from a twisting of the rings out of the coplanar configuration cannot be entirely ruled out. If the whole were to be attributed to such a cause the resultant moments of the compounds studied would range from 1.0 to 1.8 D, whilst if the  $\Delta P$  value is assumed to be about 30 c.c. in each case they would range from zero to 1.3 D. In view of the values assumed for the ring moments, the dipoles would need to be inclined at about  $170^\circ$  to lead to the results observed for most of the compounds. If each dipole were actually directed along the bisector of the angle between the linkages from the metal atom to the remainder of the molecule, however, a mere twisting of the molecule should not lead to a permanent moment. Although it is probable that the dipoles in these compounds are not directed along this axis, it is most unlikely that the permanent distortion of the molecule is sufficiently great to lead to this permanent moment.

The possibility of the molecule's undergoing a twisting vibration, however, is of some interest. If this is such that in each vibration it passes through the coplanar configuration, the  $\bar{P}_2 - [R_D]$  difference observed may validly be regarded as atom polarisation. On the other hand, if the coplanar configuration is a state of higher potential energy, so that the rings remain twisted in one sense for periods commensurate with the period of alternation of the field used in the measurements ( $10^{-6}$  sec.), the difference should be described as arising in part from a permanent dipole moment. The frequency ( $\nu$ ) of the vibrator is  $\sqrt{(k_b/4\pi^2 m_r R^2)}$ , where  $m_r$  is its effective reduced mass and  $R$  is its effective length. If these are expressed in atomic weight units and in  $\text{\AA}$ , respectively, and  $k_b$  is expressed in units of  $10^{-12}$  erg/radian<sup>2</sup>, this becomes  $\nu = 1.23 \times 10^{13} \sqrt{(k_b/m_r R^2)}$ .  $E$ , the energy hurdle which it can pass, on the average,  $10^6$  times per sec. is then given by  $e^{-E/RT} = 10^6/\nu = 0.8 \times 10^{-7} \sqrt{(m_r R^2/k_b)}$ ;  $E$  is 7.3 kcal. when  $m_r R^2$  is about 3600 and  $k_b$  is unity, and wide variations in the values of these quantities do not alter this calculated value of  $E$  by more than  $\pm 0.5$  kcal.

It is very improbable that, in the compounds studied, the energy hurdle at the coplanar configuration is as high as this. The reactions leading to the formation of the compounds occur very readily, suggesting that, in the configuration of minimum energy, the potential energy arising from repulsion between the atoms of the two rings is not great. As this cannot be far displaced from the coplanar configuration it is unlikely, therefore, that the potential energy becomes very great in the latter state. In certain types of molecule, however, where larger groups have to come into close proximity in passing through the coplanar configuration, this might occur only about  $10^6$  times per sec. In cases of this type atom and orientation polarisation merge into one another.

## EXPERIMENTAL

*Materials.*—Benzene was purified and dried as described previously.<sup>8</sup> Commercial "pure" dioxan was boiled with sodium until the metal remained bright, distilled, stored over sodium, and redistilled immediately before use.

Aluminium-acetylacetonone, prepared by Young's method<sup>9</sup> and recrystallised from benzene and light petroleum (b. p. 80–100°), had m. p. 193°: Finn, Hampson, and Sutton<sup>2</sup> give m. p. 192–193°. The ferric complex of acetylacetonone, prepared similarly and recrystallised from benzene, had m. p. 182°: Finn, Hampson, and Sutton give m. p. 181.3–182.3°. Beryllium-dibenzoylmethane, prepared by slow addition of aqueous beryllium sulphate to dibenzoylmethane in alcohol, and recrystallised from benzene and alcohol, had m. p. 214°: Booth and Pierce<sup>10</sup> give m. p. 214–215°. The ferric complex of dibenzoylmethane, prepared similarly

<sup>8</sup> Few and Smith, *J.*, 1949, 753.

<sup>9</sup> Young, *Inorg. Synth.*, 1946, 2, 25.

<sup>10</sup> Booth and Pierce, *J. Phys. Chem.*, 1933, 37, 59.

from ferric chloride, crystallised from benzene in dark red needles [Found: Fe, 7.65.  $\text{Fe}(\text{C}_{15}\text{H}_{11}\text{O}_2)_3$  requires Fe, 7.70%]. Aluminium-diethyl malonate, prepared by Titschenko's method<sup>11</sup> and recrystallised from ether, formed white needles, m. p. 95°: Titschenko gives m. p. 94.5°.

*trans*-Copper- and nickel-salicylaldoxime were prepared by adding dilute aqueous-alcoholic salicylaldoxime to solutions of copper sulphate and nickel chloride, respectively, and were recrystallised from chloroform and dioxan. *trans*-Nickel-phenylazo-*p*-cresol, prepared by Elkins and Hunter's method<sup>12</sup> and repeatedly precipitated from chloroform solution by light petroleum (b. p. 80—100°), had m. p. 216°: Elkins and Hunter give m. p. 216°. *trans*-Nickel-2-phenylazopyrrole was prepared and purified by the method of Pfeiffer *et al.*<sup>13</sup> *trans*-Copper-salicylaldehyde was prepared by dropwise addition of alcoholic salicylaldoxime to a stirred solution of copper sulphate, and was recrystallised from dioxan. *trans*-Copper-salicylidene-methylimine, prepared by Pfeiffer and Glaser's method<sup>14</sup> and recrystallised from alcohol, had m. p. 158°: Pfeiffer and Glaser give m. p. 158°.

*Copper-salicylideneaniline* was prepared by adding excess of aqueous copper sulphate to the anil in alcohol, but after 5 recrystallisations from benzene and alcohol the dielectric constants and densities of its solutions in dioxan indicated that its molecular polarisation was 264 c.c. It was therefore the *cis*-modification or a mixture containing an appreciable proportion of that form. It formed deep brown star-shaped crystals [Found: Cu, 14.0.  $\text{Cu}(\text{C}_{13}\text{H}_{10}\text{ON})_2$  requires Cu, 13.9%]. The copper-salicylidene-*p*-halogenoanilines were prepared similarly. *trans*-Copper-salicylidene-*p*-chloroaniline formed copper-brown plates from benzene [Found: Cu, 12.0.  $\text{Cu}(\text{C}_{13}\text{H}_9\text{ONCl})_2$  requires Cu, 12.1%]. *trans*-Copper-salicylidene-*p*-bromoaniline formed golden-brown plates [Found: Cu, 10.2.  $\text{Cu}(\text{C}_{13}\text{H}_9\text{ONBr})_2$  requires Cu, 10.3%]. *trans*-Copper-salicylidene-*p*-iodoaniline formed lustrous coppery plates [Found: Cu, 9.0.  $\text{Cu}(\text{C}_{13}\text{H}_9\text{ONI})_2$  requires Cu, 9.0%]. Copper-3-hydroxy-1 : 3-diphenyltriazene, prepared by Elkins and Hunter's method,<sup>15</sup> had m. p. 191—192°: Elkins and Hunter give m. p. 190—192°.

*Apparatus and Measurements.*—The dielectric constants of the solutions relative to those of the solvents were determined with a heterodyne-beat apparatus.<sup>16</sup> Some of the refractive indices were determined with a Pulfrich refractometer and the remainder with a Hilger Abbé refractometer. Specific volumes were measured with a pycnometer. All measurements were made at 25.0°.

The results from which the parameters listed in Table 1 were derived are given in Table 3, where the symbols have their usual significance. For all these compounds  $\epsilon$ ,  $\nu$ , and  $n^2$  were linear with  $w$  over the concentration range studied, and hence the slopes of the best straight lines through these values were taken as  $\alpha$ ,  $\beta$ , and  $\nu$ , respectively. The values of  $P_{2\infty}$  and  $[R_D]$  deduced from these parameters were checked by comparison with the values of  $P_2$  and  $[R_D]$  calculated from the data for each concentration. There appeared to be no systematic variation of either  $P_2$  or  $[R_D]$  with concentration.

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<sup>11</sup> Titschenko, *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 784.

<sup>12</sup> Elkins and Hunter, *J.*, 1935, 1598.

<sup>13</sup> Pfeiffer, Hesser, Pfitzner, Scholl, and Thielert, *J. prakt. Chem.*, 1937, **149**, 217.

<sup>14</sup> Pfeiffer and Glaser, *ibid.*, 1939, **153**, 265.

<sup>15</sup> Elkins and Hunter, *J.*, 1938, 1346.

<sup>16</sup> Few, Smith, and Witten, *Trans. Faraday Soc.*, 1952, **48**, 211.